

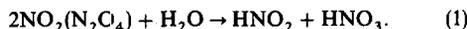


DISCUSSION

LABORATORY STUDY OF NO₂
REACTION WITH DISPERSED AND
BULK LIQUID WATER*

Recently Novakov and his colleagues (Bambauer *et al.*, 1994) have reexamined the rate of the reactive uptake of nitrogen dioxide (NO₂) by water under laboratory conditions. Two types of gas-liquid contactor were employed, a bubbler, similar to that employed in our earlier work (Lee and Schwartz, 1981a), and a cloud chamber, in order to examine the applicability of kinetic information determined in bulk liquids to a dispersed system such as a cloud. We commend Bambauer *et al.* (1994) for undertaking this study and recognize the difficulty of the experiment, especially in maintaining constant conditions in the cloud chamber for the rather long periods (typically an hour) required to collect sufficient amounts of cloudwater to permit chemical analysis. We nonetheless appreciate the advantage afforded by direct comparison between reaction rate measured in the cloud-chamber reactor with that measured in the bubbler in confirming the applicability of "bulk" rate laws to reactions in dispersed clouds. The expectation of course is that the rates would be equal. In fact the reaction rate was found to be substantially greater in the cloud-chamber reactor, leading Bambauer *et al.* (1994), to conclude that different mechanisms govern the reaction rate in the bulk reactor vs in the dispersed system. Here we suggest that the rate measured in the cloud-chamber reactor may have been enhanced artificially because of nonuniform concentration distribution of the reagent gas NO₂ together with the second-order dependence of the rate on NO₂ concentration. Consequently the conclusion by Bambauer *et al.* (1994) that the rate expression determined using a bulk reactor is inapplicable to evaluation of the rate of this reaction in clouds in the ambient atmosphere may not be warranted.

By way of background, we note that the reactive dissolution of NO₂ into liquid water is a process of a major industrial importance in the manufacture of nitric acid. At NO₂ concentrations characteristic of this process NO₂ and/or its dimer N₂O₄ dissolve in water and rapidly react to form nitrous and nitric acids:



In view of the strong thermodynamic driving force for reaction (1) and the commonly observed rapid rate of reaction, this reaction had long been presumed to proceed rapidly also in liquid water clouds in the atmosphere.

In order to determine the solubility and rate constants necessary to evaluate the rate of reaction (1) in the ambient atmosphere, we conducted a laboratory study of the rate of this reaction at low partial pressures, $p_{\text{NO}_2} = 0.1\text{--}800 \mu\text{atm}$ (Lee and Schwartz, 1981a). That study consisted of passing NO₂ (in nitrogen or in air) through water as finely dispersed bubbles produced by passing the gas stream through a glass frit that comprised the bottom surface of a vessel containing the liquid. The small bubble size together with the vigorous mixing induced by the bubble swarm promoted efficient

phase mixing, the rate of which could be independently characterized in terms of a stochastic rate coefficient k_m . The rate of reaction was measured continuously by monitoring the rate of increase of electrical conductivity of the solution, and the reaction stoichiometry was confirmed by analysis of the final solution composition.

From the dependence of the reaction rate on NO₂ partial pressure and k_m , it was possible to infer separately Henry's law coefficient for physical dissolution of NO₂ in water H_{NO_2} , and the rate law of reaction (1), which was found to be second order in NO₂. The values of H_{NO_2} and of the reaction rate coefficient are consistent with values of these quantities inferred from a review of the literature on thermodynamics and kinetics of the nitrogen oxide-oxyacid system (Schwartz and White, 1981, 1983). Subsequent studies by others have borne out the rate expression obtained in our study (e.g. Cape *et al.*, 1993).

Knowledge of the values of H_{NO_2} and k_1 determined in this way allowed evaluation of the rate of reaction (1) in liquid water clouds in the ambient atmosphere as

$$R_1 = k_1[\text{NO}_2(\text{aq})]^2 = k_1 H_{\text{NO}_2}^2 p_{\text{NO}_2}^2 \quad (2)$$

where the second equality holds under phase mixed conditions. The requirements for satisfaction of the phase mixed condition can be evaluated and shown to be met under representative atmospheric conditions. Evaluations of R_1 for representative conditions indicate that this reaction is quite slow, owing to the second-order kinetics and the low Henry's law solubility of the gas (half life of gas-phase NO₂ ~ 1 month at $p_{\text{NO}_2} = 1 \mu\text{atm}$ to ~100 yr at 1 natm, for cloud liquid-water content $1 \text{ cm}^3 \text{ m}^{-3}$; Lee and Schwartz (1981b)). The expectation of slow reaction in clouds based on this laboratory study is consistent with the common field observation of NO₂ present in persistent liquid-water clouds (e.g. Daum *et al.*, 1984; Fuzzi *et al.*, 1994; Colville *et al.*, 1994).

In the study of Bambauer *et al.* (1994), NO₂ was first introduced into a cloud chamber and exposed to a suspension of droplets produced when a humidified air stream was mixed with a cold dilution air stream. The rate of reaction was determined from the concentration of dissolved NO₃⁻ and/or NO₂⁻ in collected liquid water and the contact time, ca. 3 min. A second independent measurement of the rate was achieved by passing the gas exiting the cloud chamber first through a filter (to remove any suspended particles) and then into a bubbler reactor, evidently similar to that used in our study, with determination of reaction rate from analysis of the composition of the solution after a given contact time. With the bubbler reactor Bambauer reported, rates that they indicated were consistent with those reported in our earlier study, taking into account plausible differences in the mass-transport properties of the two reactors, since the mixing rate coefficient characterizing their reactor was not determined. In contrast, with the cloud-chamber reactor, Bambauer *et al.* (1994) found aqueous concentrations that corresponded to reaction rates much greater than were observed in the bubbler reactor (500- to 1700-fold) or than would be expected based on equation (2) (30- to 400-fold, Table 1). Based on an approximate linear dependence of measured rate on NO₂ partial pressure in the cloud chamber, Bambauer *et al.* ascribed this rate to a first-order reaction, which they attributed either to mass-transport limitation reducing the reaction order (from the expected second order to first order), or to a different mechanism for reaction in or on cloud droplets than in the bulk.

* Bambauer A., Brantner B., Paige M. and Novakov T. (1994) *Atmospheric Environment* **28**, 3225-3232.

Table 1. Comparison of reaction rates (column 5) derived from data of Bambauer *et al.* (1994) for cloud-chamber reactor (columns 1–3) with rates (column 6) calculated according to second-order reaction [equation (2)] with $H_{\text{NO}_2} = 7 \times 10^{-3} \text{ M atm}^{-1}$ and $k_1 = 1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Lee and Schwartz, 1981a)

Average P_{NO_2} (μatm)	LWC ($\text{cm}^3 \text{ m}^{-3}$)	$\{\text{NO}_3^-\}$ ($\mu\text{mol m}^{-3}$)	$[\text{NO}_3^-]$ ($\mu\text{mol l}^{-1}$)	R_{meas} (nM s^{-1})	R_{calc} (nM s^{-1})	C_1/C_{avg}	$R_{\text{meas}}/R_{\text{calc}}$
3.16	1.89	0.51	270	1910	48.9	158	39
3.06	1.81	0.66	365	2580	45.9	163	56
2.76	1.36	0.34	250	1770	37.3	181	47
2.56	2.39	0.44	184	1300	32.1	195	41
1.55	2.27	0.3	132	935	11.8	323	79
1.51	1.29	0.24	186	1316	11.2	331	118
0.86	0.75	0.11	147	1037	3.62	581	286
0.75	1.54	0.14	91	643	2.76	667	233
0.52	3.14	0.17	54	383	1.32	962	289
0.48	1.2	0.08	67	472	1.13	1040	418
0.46	2.94	0.11	37	265	1.04	1090	255

Note: R_{meas} is evaluated as the concentration of aqueous nitrate $[\text{NO}_3^-]$ divided by the contact time, here taken as 141 s, evaluated from the reactor volume 30.2 l and the flow rate 12.8 l min^{-1} . The concentration ratio C_1/C_{avg} is taken as the ratio of the inlet partial pressure of NO_2 , $500 \mu\text{atm}$, to the average NO_2 partial pressure in column 1.

In our opinion neither of these explanations seems plausible. The mass-transport explanation seems ruled out by the fact that the rate is in fact much *greater* than would be calculated based on assumed Henry's law saturation, not less, as would be the case for mass-transport limitation. In any event, the rather fine dispersion would promote mass transport, not inhibit it. Likewise, it is difficult to postulate a chemical mechanism that would be first order in NO_2 , especially given the roughly comparable concentrations of NO_2^- and NO_3^- observed by Bambauer *et al.* in the collected cloudwater samples. (The depletion of NO_2^- noted by Bambauer *et al.* at higher acidities seems reasonably ascribed to volatility of HNO_2 .) We are thus motivated to explore alternative explanations that might account for the observations of Bambauer *et al.* that are consistent with present understanding of the mechanism and kinetics of this reaction.

A possible explanation for the anomalously high rates observed with the cloud chamber, is suggested by an observation of Bambauer *et al.* with reference of their Fig. 1, that "determination of the rate for the reaction between NO_2 and cloud droplets... is difficult because of the unknown NO_2 concentration gradient resulting from the manner in which the NO_2 is introduced into the chamber". Reference to that figure shows that rather than the NO_2 being introduced into the cloud chamber at the partial pressure desired for a given run (0.5 to $3 \mu\text{atm}$), it was introduced at the partial pressure of the NO_2 source ($500 \mu\text{atm}$), with dilution occurring within the chamber itself. Since according to equation (2) the rate of reaction (1) is second order in NO_2 , the rather high inlet partial pressures could lead to quite rapid reaction prior to dilution to the final partial pressure. We thus tried to assess the effect on the observed average rate due to reaction occurring near the region of the NO_2 inlet prior to complete dilution of NO_2 to its final partial pressure. If substantial reaction occurs in the inlet region, then this might trivially account for the observed apparent high reaction rates obtained with the cloud-chamber reactor.

In order to assess the magnitude of this effect we formulated a model in which the reactor volume is conceptually divided into two regions of unequal volume, each containing a fixed fraction of the reagent. Here the volume fraction f_1 , representing the region in the vicinity of the NO_2 inlet, is much smaller than the remainder of the reactor volume $f_2 (= 1 - f_1)$ and contains a much higher reagent concentration. Because of the second-order nature of the reaction, the rate of reaction averaged over the entire reactor volume is considerably greater than would be the case if the reagent

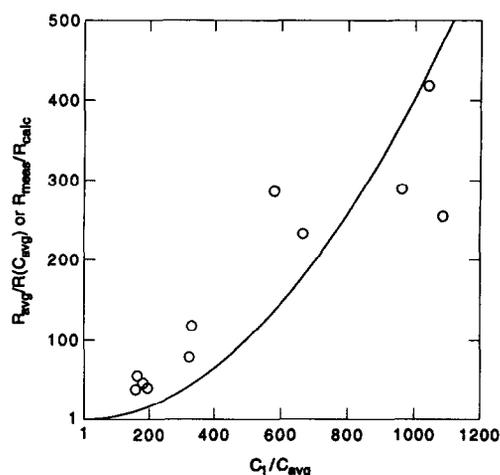


Fig. 1. Ratio of rate of second-order reaction for a nonuniform reagent concentration averaged over a reactor volume to that evaluated for the average reagent concentration. Curve denotes results of two-box model calculation as described in the text plotted as a function of the ratio of the reagent concentration in the small, high concentration box to the average concentration. Points denote ratio of the average reaction rate, as evaluated from the measurements presented by Bambauer *et al.* (1991), to rate calculated according to equation (2) with H_{NO_2} and k_1 determined by Lee and Schwartz (1981a), plotted as a function of the ratio of the inlet partial pressure to the average reagent partial pressure in their cloud-chamber reactor.

were uniformly distributed. The enhancement of mean reaction rate is displayed in Fig. 1 as a function of the ratio of the concentration in the smaller, higher concentration subregion C_1 to the mean concentration C_{avg} . Variation of the ratio of the inlet concentration to the mean concentration (corresponding to changing the inlet flow rate and hence the mean partial pressure of the NO_2 reagent in the experiment) is achieved in the model by varying the volume fraction f_1 , which here ranges from 2×10^{-6} at $C_1/C_{\text{avg}} = 200$ to 4×10^{-7} at $C_1/C_{\text{avg}} = 1000$. There is only a single adjustable parameter in the calculation, namely the fraction of reagent

